

Final Report

FLEXIBLE EMI SHIELDING MATERIALS USING CONDUCTING COPOLYMERS

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I. INTRODUCTION

Tactical shelters used by the Army are constructed from metallic sheet materials, which provide high electromagnetic shielding interference (EMI) protection. Because these materials provide no flexibility, they will not meet the future needs of the Army. There is therefore a need for materials with high electrical shielding characteristics in a light weight, tent-like, flexible fabric to enable a rapidly erectable and collapsible capability. The work described here-in involves the research and development of flexible EMI shielding materials using metallic mesh or knitted wire mesh sandwiched between two sheets of an electrically conducting copolymer which is elastomeric in nature. The rationale for using a conducting polymer matrix is that a perforated barrier (wire screen) cannot give better shielding than a homogeneous one, everything else being equal.

II. OBJECTIVES

The primary objective of the program was to generate flexible material concepts, fabricate prototypes, and determine feasibility of the concept by testing the prototypes for EMI shielding effectiveness (SE), flexibility, ruggedness, and environmental durability. As outlined in the Phase I proposal, the specific technical objectives were:

1. Determine the monomer reactivity ratios for the copolymerization of isobutylene with aniline, pyrrole and 3-methylthiophene in methylene chloride at -78°C.
2. Using the values for the reactivity ratios, synthesize and characterize copolymers with long segments of both monomeric units.
3. Construct prototype laminates
4. Evaluate prototypes.

A significant goal of Phase I was to demonstrate shielding higher than 40 dB at 150 kHz in the Magnetic Field.

III. RESULTS AND DISCUSSION

The program was organized along four main tasks as outlined in the technical objectives.

Determination of Reactivity Ratios

Copolymerizations of isobutylene with aniline, pyrrole and 3-methylthiophene were carried out using anhydrous ferric chloride as oxidant in methylene chloride in batch processes under nitrogen with magnetic stirring in a four neck flask immersed in Dry Ice-Acetone. After 2 hours at -78°C, the yields of copolymer were low, with no significant increase with time.

When aniline, pyrrole and 3-methylthiophene were homopolymerized at -78°C using the same conditions, the conductivity of the polymer was identical to that prepared at -5°C. In view of this, subsequent copolymerizations were carried out between -5 and -10°C; isobutylene boils at -7°C. The yields of copolymer, however, did not increase with the higher temperature. Because of this, copolymerization using other vinyl monomers was

investigated. A discussion of the copolymerization reaction follows and reactivity ratios are reported in Table 1.

According to a widely accepted mechanism (1), the initial step in the polymerization of a resonance stabilized aromatic molecule, M_1 , is the generation of its radical cation. Chain propagation then proceeds by reaction of two radical cations, pairing the spins and elimination of two protons to form the neutral dimer. Chain growth continues by oxidation of the dimer to form another radical cation with subsequent coupling, proton loss, and oxidation. If these radical cations can add to olefinic double bonds to generate other radical cations, copolymerization with a vinyl monomer, M_2 , is plausible.



The oxidation of M_2 to form its radical cation occurs at much higher oxidation potentials. In the case of isobutylene, for example, oxidation occurs at 1.8 V compared to 1.0 V (versus an Ag/Ag⁺ reference electrode) for the present system.



Hence, there are four different propagation rate constants, defined by eq. 3-6.

| Reaction | Rate | |
|--|----------------------------|-------|
| $-M_1^+ + M_1^+ \rightarrow -M_1^+M_1^+$ | $k_{11}[-M_1^+][M_1^+]$ | eq. 3 |
| $-M_1^+ + M_2 \rightarrow -M_1M_2^+$ | $k_{12}[-M_1^+][M_2]$ | eq. 4 |
| $-M_1M_2^+ + M_1^+ \rightarrow -M_1M_2^+M_1^+$ | $k_{21}[-M_1M_2^+][M_1^+]$ | eq. 5 |
| $-M_1M_2^+ + M_2 \rightarrow -M_1M_2M_2^+$ | $k_{22}[-M_1M_2^+][M_2]$ | eq. 6 |

It is interesting to note that eq. 4 represents the initiation of radical-cationic polymerization of a vinyl monomer and eq. 6 is the ensuing propagation in which the growing species is a hydrocarbon radical cation for the first time.

The ability to predict both the average composition of the copolymer formed at any instant in the copolymerization and the sequence distribution of monomer units is desirable. There is therefore a need to determine the monomer reactivity ratios, r_1 and r_2 , which are the ratios of rate constants for homopropagation and heteropropagation.

$$\text{Thus, } r_1 = k_{11}/k_{12} \text{ and } r_2 = k_{22}/k_{21}.$$

It is necessary here to assume:

1. The rate of coupling of radical cations depends only on the nature of the endgroup on the radical cation chain.
2. The concentrations of $-M_1^+$ and $-M_2^+$ must each remain constant.
3. The rate of proton loss is faster than both oxidation and coupling.

Combining these assumptions with two equations for the rates of disappearance of each monomer and with an equation for the disappearance of M_1^+ yields the copolymer equation:

$$d[M_1]/d[M_2] = [M_1]/[M_2] (r_1[M_1][M_2]) / ([M_1] + r_2[M_2]) \quad \text{eq. 7}$$

The resonance stabilized aromatic molecule that polymerizes to give a conductive polymer is defined here as M_1 and the vinyl monomer is M_2 . The mole fractions of M_1 and M_2 in the initial monomer feed are denoted as f_1 and f_2 and similarly, the mole fractions of M_1 and M_2 in the copolymer are F_1 and F_2 , respectively.

Each copolymer was prepared by adding the comonomer feed to a mixture of anhydrous FeCl_3 and solvent at 5°C under N_2 in a 500 ml four-necked flask equipped with thermometer, gas inlet, magnetic stirrer and immersed in an ice-water bath. For copolymerization of aniline in CH_2Cl_2 , the charge consisted of 200 ml solvent, 22.8 g. FeCl_3 , 5 g. aniline and the required amount of M_2 . For the copolymerization of pyrrole, the charge was 200 ml CH_2Cl_2 , 4.05 g. FeCl_3 , 0.67 g. pyrrole and the required amount of M_2 . And for the copolymerization of 3-methylthiophene, the charge consisted of 200 ml CH_2Cl_2 , 35.68 g. FeCl_3 , 5 g. 3-methylthiophene and the required amount of M_2 .

After the reaction was allowed to proceed to low conversion, the copolymer was collected by filtration. The precipitates from the pyrrole and 3-methylthiophene copolymerizations were placed separately in beakers containing 500 ml of methanol and stirred for several minutes. The product in each case was then collected after filtration and washing with methanol. The precipitate from the aniline copolymerization was stirred in water and the wet filter cake was converted to its emeraldine base (2). All chemicals (99+ % purity) were obtained from Aldrich Chemical and used as received. The composition of all copolymers was determined from elemental analyses performed by Galbraith Laboratories, Inc., Knoxville, TN. The copolymers which were isolated are insoluble in solvents in which the vinyl homopolymers are soluble, indicating that the vinyl units are chemically incorporated.

Figure 1 shows the structure of the copolymers and Figure 2 shows plots of copolymer composition versus comonomer feed for three successful copolymerizations of styrene with aniline, pyrrole and 3-MT.

Values of reactivity ratios with the standard error obtained from a least squares treatment of the data are reported in Table 1. The scatter is a result of errors in the elemental analysis, the presence of impurities such as residual solvent and monomer in the copolymer, and the removal of soluble fractions of oligomers. In addition, there are uncertainties inherent in the treatment of the data. These occur when r_1 and r_2 differ widely. Further, the points where F_1 is less than 0.2 and greater than 0.8 have a large effect on both the slope and intercept.

As seen in Table 1, there are copolymerizations where $r_1 \approx r_2 \approx 1$, within experimental limits. Here $k_{11} = k_{12}$ and $k_{22} = k_{21}$ and there is little or no selectivity by a polymer radical cation for either monomer or radical cation, and the insertion of monomer into the copolymer is random with $F_1 \approx f_1$. In the case of aniline and styrene in nitromethane or nitrobenzene, the copolymer consists mostly of styrene units.

Table 1. Monomer Reactivity Ratios for the Copolymerization of Aniline, Pyrrole and 3-Methylthiophene with Styrene and Vinyl Acetate. Numbers in parentheses give the standard error.

| M ₁ | M ₂ | r ₁ | r ₂ | Solvent | Temp. (°C) |
|----------------|----------------|----------------|----------------|---|------------|
| Styrene | | 0.26 (0.15) | 20.98 (10.37) | CH ₃ NO ₂ | 5 |
| Aniline | Styrene | 0.73 (0.08) | 0.46 (0.25) | CH ₂ Cl ₂ | 5 |
| Pyrrole | Styrene | 1.21 (0.10) | 1.78 (0.36) | CH ₂ Cl ₂ | 5 |
| 3-MT | Styrene | 1.48 (1.85) | -0.05 (2.18) | CH ₂ Cl ₂ | 5 |
| 3-MT | Styrene | 1.50 (0.67) | 1.66 (1.36) | C ₆ H ₅ NO ₂ | 5 |
| 3-MT | Styrene | 2.93 (0.36) | 1.40 (0.11) | C ₆ H ₅ NO ₂ | 30 |
| 3-MT | Vinyl Acetate | 3.47 (0.59) | 0.39 (0.43) | C ₆ H ₅ NO ₂ | 5 |
| 3-MT | Vinyl Acetate | 0.59 (0.004) | 0.34 (0.002) | C ₆ H ₅ NO ₂ | 30 |

Synthesis and Characterization of Copolymers

The copolymers and homopolymers lost their conductivity upon exposure to water and elevated temperatures necessary for lamination. This was a serious problem which had to be solved before laminates could be constructed and evaluated for magnetic shielding effectiveness. It was hoped that copolymerization would impart conventional processability to conducting polymers but to date we have no evidence to support this. Since our initial experiments, we have improved the stability of the aniline copolymers by replacing the chloride counterion with long chain alkyl sulfonate counterions as described by Heeger et al (4). Figure 3 shows the TGA of an experimental polyaniline and Figure 4 shows the TGA of a commercially available polyaniline which exhibits exceptional stability.

Heeger indicated that the conductivity of polyaniline alkyl sulfonates could be increased by one order of magnitude by adding m-cresol. And, indeed, the conductivity of the experimental polyaniline increased from 4 S/cm to 40 S/cm after treatment with m-cresol. This is a significant finding because EMI SE increases with conductivity.

Heeger also reported that blending of small quantities of conducting polyaniline with vinyl polymers produces an alloy with the conductivity of polyaniline and the physical properties of the vinyl polymer.

Results of reactivity ratio determinations indicate $r_1 \approx r_2 \approx 1$, within experimental limits. This means that there is little or no selectivity by a polymer radical cation for either monomer or radical cation, and the insertion of monomer into the copolymer is random with the composition of monomer units in the copolymer equal to that in the comonomer feed.

This random insertion of vinyl monomer units into the copolymer disrupts the conjugation necessary for conductivity and as a result there is a dramatic decrease in conductivity. Thus it was necessary to prepare copolymers with long sequences of the aromatic monomer for conductivity and long blocks of vinyl monomer for processibility. Figure 5 shows a plot of conductivity versus composition for aniline styrene copolymers. It is clear that copolymerization lowers the conductivity and that we were unsuccessful in our efforts to prepare a material with long blocks of both monomers. Because 500 grams of copolymer were needed to prepare one sample for EMI SE, it was unlikely that adequate quantities of copolymer would be readily available for compression molding of laminates for testing using oxidative polymerization. For instance, large amounts of oxidant (20 grams) and (50 ml) of solvent were used to obtain 10 grams of the aniline-styrene copolymer. In light of this, and the availability of large quantities of a blend of polyaniline and polyvinyl chloride, the synthesis program was discontinued.

Construction of Laminates

A 13.5" x 13.5" x 0.125" stainless steel mold, and 20 pounds of Incoblend (Polyaniline/Polyvinyl Chloride blend) were purchased. But efforts to find a compression molding press to prepare specimens were unsuccessful. It was necessary to prepare sheets by calendering using a two roll but the largest width was 7". Two sheets were therefore adhesively bonded in order to obtain the 13.5" width.

Using the 6" x 6" Carver Press in our laboratory, we prepared laminates by pressing a 100 x 100 copper mesh sandwiched between two sheets of Incoblend at 150°C for 5 minutes at 1,000 psi. The laminate was flexible, rugged and environmentally stable.

Some laminates were prepared by fusing a plastisol containing Versicon, which is a commercially available polyaniline; Geon 121, a PVC dispersion resin; Mark 2077 LV, a stabilizer; and diethyl phthalate. These were less conductive than Incoblend. Figure 6 is a plot of conductivity versus composition of Versicon/PVC mixtures. It is noteworthy that the conductivity decreases with decreasing concentration of polyaniline and this contradicts Heeger, who insists that a blend of 2% polyaniline and 98% polymethyl methacrylate is as conductive as polyaniline.

The other important aspect of this task was the selection of the wire mesh. A search of the commercial literature was undertaken to identify and select materials that would offer SE values above 40 dB at 150 kHz in the H-field. At first, this seemed to be a minor task since SE values can be estimated based on calculations. Moreover, the manufacturers of EMI shielding meshes report test results. Unfortunately, the published EMI SE values are based on a 5" x 5" aperture. Typical values are reported in Table 2 below.

Table 2. EMI SE Values of some Commercially Available Wire Meshes

| MATERIALS | Diameter | H-FIELD, 100 kHz |
|-------------------------------|----------|------------------|
| Knitted Wire Mesh | | dB |
| Silver-Plated Brass | 0.005" | 80+ |
| Tin-Plated Phosphor Bronze | 0.0045" | 80+ |
| Tin-Coated Copper-Clad Steel | 0.0045" | 80+ |
| Monel (a Nickel-Copper alloy) | 0.0045" | 60 |
| Aluminum | 0.005" | 60+ |

The only knitted wire mesh available to us was 6" wide. Plain weave meshes available in widths exceeding 13.5" included stainless steel, brass, bronze, plain steel, monel, pre-galvanized, post-galvanized, aluminum and copper. Meshes of metals with very high permeabilities, such as Supermalloy, Permalloy, Rhometal and Mumetal, were unavailable. Copper was selected because published calculated values of SE agreed with experimental results. A 12 x 12 mesh and a 100 x 100 mesh were selected.

Table 3 presents data on actual measurements of EMI SE tests on different copper meshes along with the predicted values. The data obtained from the literature (5) came from 5 different sources, totalling 72 series of measurements. Near H-field test distances were 30 cm, 4.4 cm and 3.8 cm depending on the report. The important point here is that the magnetic shielding increases with the mesh size.

Table 3. Comparison of Measured Data vs. Calculated Values from Reference 5

| Mesh Size | SE (Magnetic) Calculated | SE (Magnetic) Measured (Min-Max) |
|-----------|-----------------------------|-------------------------------------|
| 2/inch | 21 dB | 15-19 dB |
| 16/inch | 39 dB | 33-41 dB |
| 22/inch | 45 dB | 44-52 dB |
| 60/inch | 54 dB | 40-62 dB |

Evaluation of Laminates

A 10 pound batch of Incobblend, obtained from Americhem, was calendered on a two-roll mill by Rehau, Inc. at its laboratory in Virginia. Sets of two 6.75" x 13.5" x 0.125" sheets were adhesively bonded to produce 13.5" x 13.5" x 0.125" sheets which were sent

to Diversified Technologies for EMI shielding tests. Photographs of the test set-up are shown in Figure 7 and the test results are reported below in Tables 4 and 5.

Table 4. MIL-STD 285 Shielded Effectiveness Test Results

| Sample #/Attenuation, db | Magnetic Field | | Electric Field | | Plane Wave | |
|--------------------------|----------------|--------|----------------|-------|-----------------|------------------|
| | 200KHz | 150KHz | 1MHz | 18MHz | 400MHz Vert. | Horiz. Polar. |
| Incoblend-1 | 0 | 68 | 62 | 19 | 37 | 37 |
| Incoblend-2 | 0 | 66 | 60 | 17 | 37 | 43 |
| Incoblend-3 | 0 | 62 | 60 | 19 | 43 | 45 |
| Incoblend-4 | 0 | 63 | 58 | 15 | 41 | 45 |
| Incoblend-3/12 Cu mesh | 25 | 66 | 77 | 54 | 43 | 43 |
| Incoblend-3/100 Cu mesh | 25 | 60 | 71 | 64 | 48 | 46 |
| PVC/12 Cu mesh | 26 | 62 | 64 | 60 | 37 | 34 |
| PVC/100 Cu mesh | 25 | 66 | 77 | 57 | 41 | 41 |

Legend:

12 Cu mesh - 0.023" diameter, 0.0603" opening, 51.8% open area and 42.2 lb per 100 square feet.

100 Cu mesh - 0.0045" diameter, 0.0055" opening, 30.3% open area and 14.2 lb per 100 square feet.

It is clear that the conducting polymer contributes no shielding in the magnetic field at 200 KHz and that a metallic component is required. The low shielding at 18 MHz from the conducting polymer alone increases with the use of the copper mesh but the magnitude is the same as that obtained with polyvinyl chloride and the mesh. The copper mesh increases the shielding offered by the conducting polymer in the plane wave region and the values are slightly higher than those with PVC and the plain weave square mesh. The fact that there is no apparent difference between the attenuation obtained with either mesh indicates a serious problem with the method of testing. The magnitude of the problem is amplified below in Table 5 which shows no increase in SE with increasing layers of the 100 mesh.

Table 5. MIL-STD 285 Shielded Effectiveness Test Results

| Sample #/Attenuation, db | Magnetic Field | | | | Plane Wave | |
|--------------------------------|----------------|-------|--------|--------|------------------------------|------------------|
| | 150 KHz | 1 MHz | 10 MHz | 15 MHz | 1,000 MHz Vert. Polar. | Horiz. Polar. |
| I-3/12 Mesh | 25.5 | 32 | 44 | 41 | 35 | 39 |
| I-3/100 Mesh | 26.5 | 34 | 56 | 58 | 31 | 48 |
| 12 Mesh | 25.5 | 32 | 44 | 44 | 45 | 54 |
| 100 Mesh | 22.5 | 31 | 42 | 42 | 33 | 50.5 |
| I-3/100 Mesh/100 Mesh | 26 | 36 | 50 | 46 | 53 | 51 |
| I-3/100 Mesh/100 Mesh/100 Mesh | 27 | 39 | 54 | 51 | 57 | 46 |
| 100 Mesh/100 Mesh | 29 | 39 | 54 | 51 | 51 | 60 |
| 100 Mesh/100 Mesh/100 Mesh | 28 | 39 | 54 | 51 | 52 | 49 |

It is obvious that there are problems and shortcomings with MIL STD 285 as a method for evaluating magnetic shielding effectiveness. The attenuation offered by the 100 mesh should be higher than that of the 12 mesh. Increasing the number of layers of mesh should increase the shielding. An absolute method is needed.

IV. CONCLUSIONS

On the basis of the preceding results, Gumbs Associates, Inc. concludes the following:

1. Isobutylene does not readily copolymerize with aniline, pyrrole or 3-methylthiophene.
2. Styrene copolymerizes easily with aniline, pyrrole and 3-methylthiophene. The insertion of monomer into the copolymer is random with $F_1 \approx f_1$. It is difficult to control the sequence distribution on monomer units in the copolymer.
3. A commercial polyaniline/polyvinyl chloride alloy with an electrical conductivity of 2-4 S/cm possesses adequate properties for the construction of flexible laminates with a 100 x 100 copper mesh sandwiched between its sheets. It is believed that adequate EMI SE at 150 kHz may be possible with one layer of mesh.
4. The conductivity of the alloy increases by one order of magnitude after treatment with m-cresol. An increase in EMI SE is anticipated.
5. The EMI SE test results show no significant increase in the magnetic shielding

with the use of the conducting polymer over an insulating polymer as a binder in the laminate.

6. MIL STD 285 as performed during Phase I was not sensitive in detecting changes in attenuation at low frequencies in the H-Field based on the fact that a 12 x 12 Cu mesh produced the same shielding as a 100 x 100 Cu mesh. In addition, the observed shielding with one layer of 100 x 100 mesh was the same as that with two and three layers. Leakage around the joints and in the shielded room is probably responsible for this. An absolute test method is needed to adequately characterize the magnetic shielding of flexible laminates.
7. The use of meshes of metals with very high permeabilities in laminates may yield higher shielding than that from the Cu mesh. But such meshes are not available.

V. APPENDIX

Legends of Figures

Fig. 1: Proposed Structures of Vinyl Copolymers of (a) aniline, (b) 3-methylthiophene, and (c) pyrrole.

Fig. 2: Instantaneous composition of copolymer (F_1) as a function of monomer composition (f_1) for styrene copolymers of aniline (●), pyrrole (○), and 3-methylthiophene (▲).

Fig. 3: TGA curve of polyaniline sulfosuccinate.

Fig. 4: TGA curve of commercial polyaniline.

Fig. 5: Conductivity versus F_2 for styrene copolymer of aniline.

Fig. 6: Conductivity versus composition of blends of Versicon and Polyvinyl Chloride.

Fig. 7: Photographs of EMI SE Test Set-up.

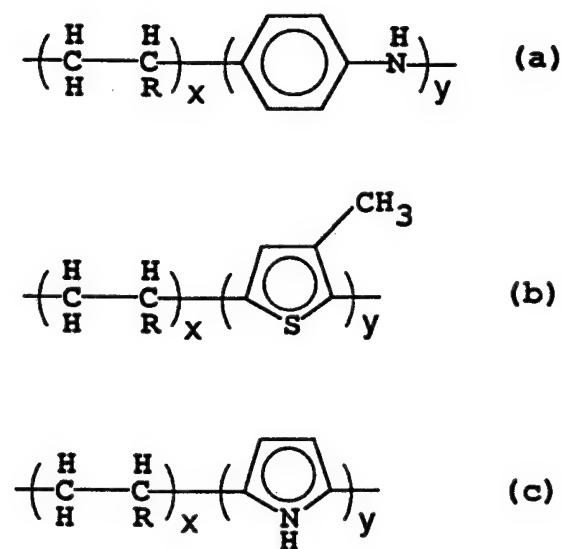


Figure 1. Proposed Structures of Vinyl Copolymers of (a) aniline, (b) 3-methylthiophene, and (c) pyrrole

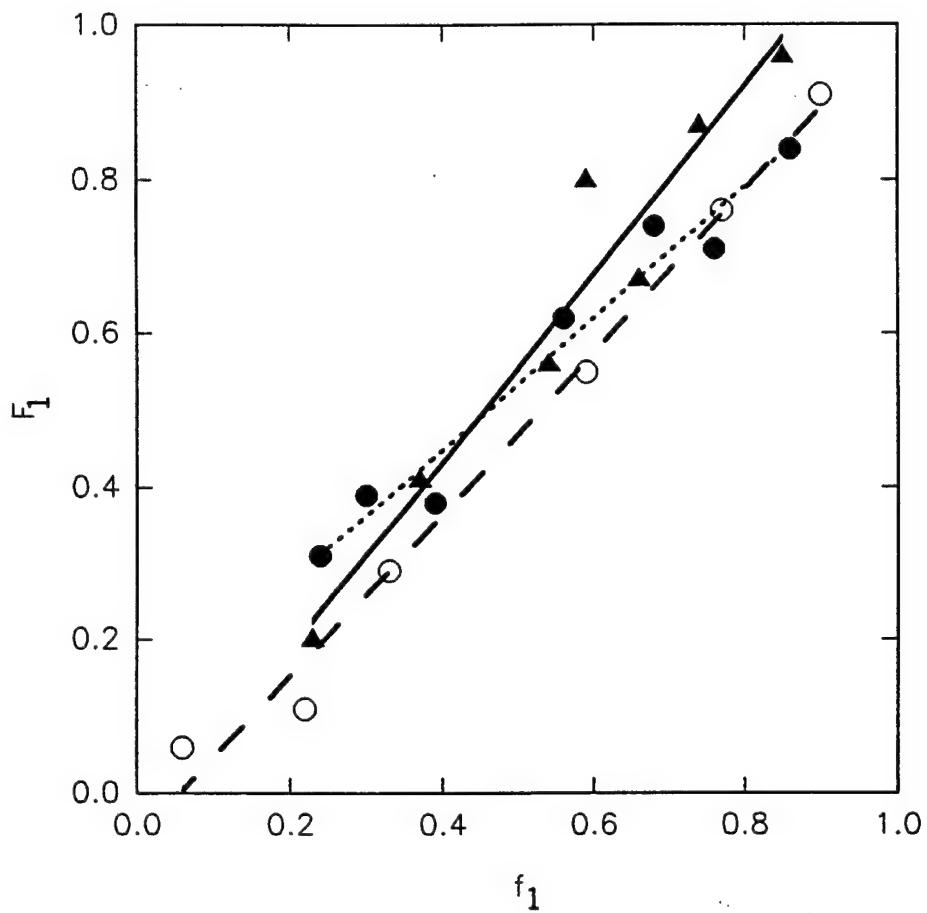


Figure 2. Instantaneous composition of copolymer as a function of monomer composition for styrene copolymers of aniline, pyrrole, and 3-methylthiophene.

Sample: DOSPA3
Size: 10.6890 mg
Method: TGA-CH
Comment: 10 C/MIN 30 C to 700 C N2

TGA

File: D053.03
Operator: CHEN
Run Date: 07/05/93 03: 35

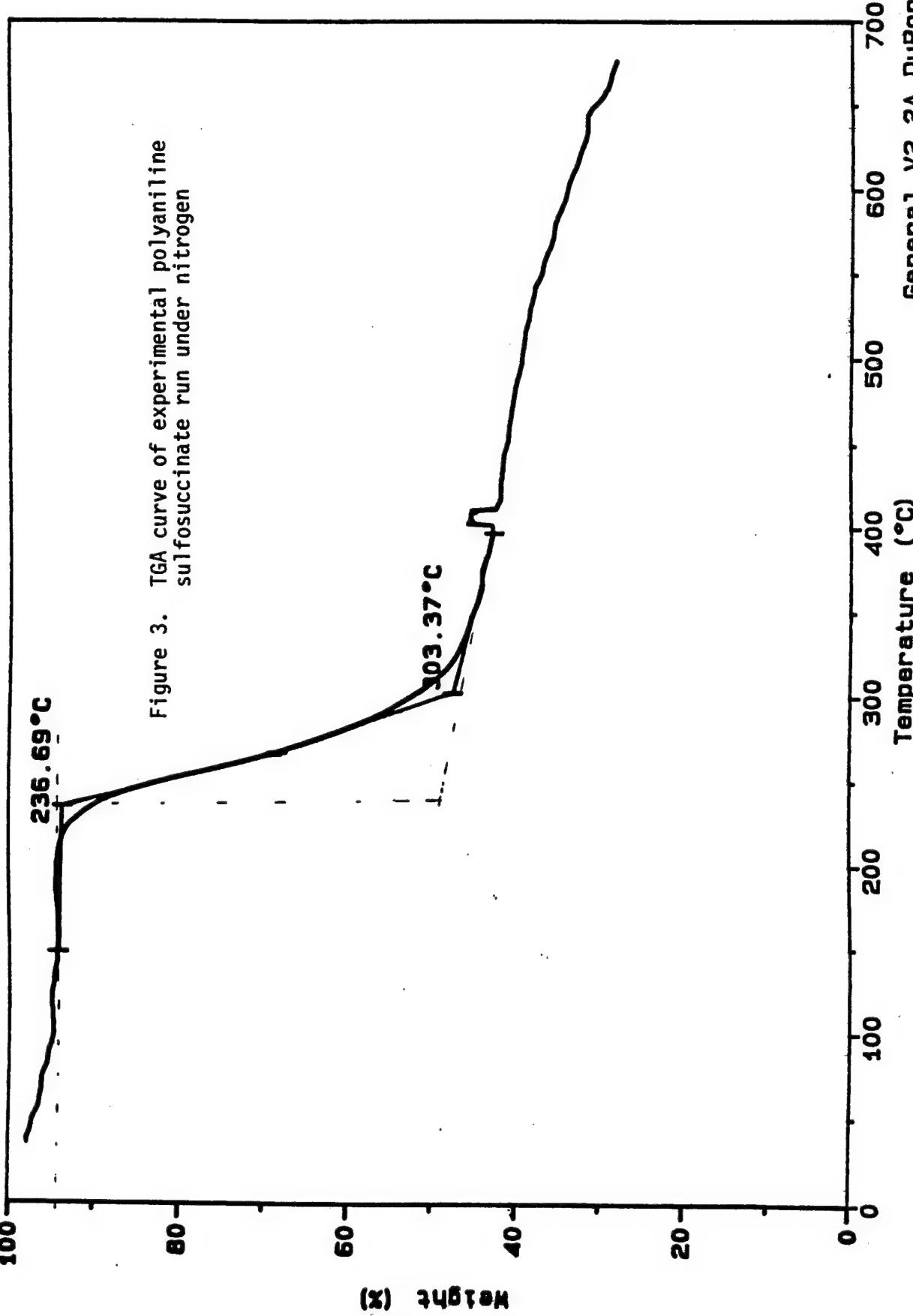
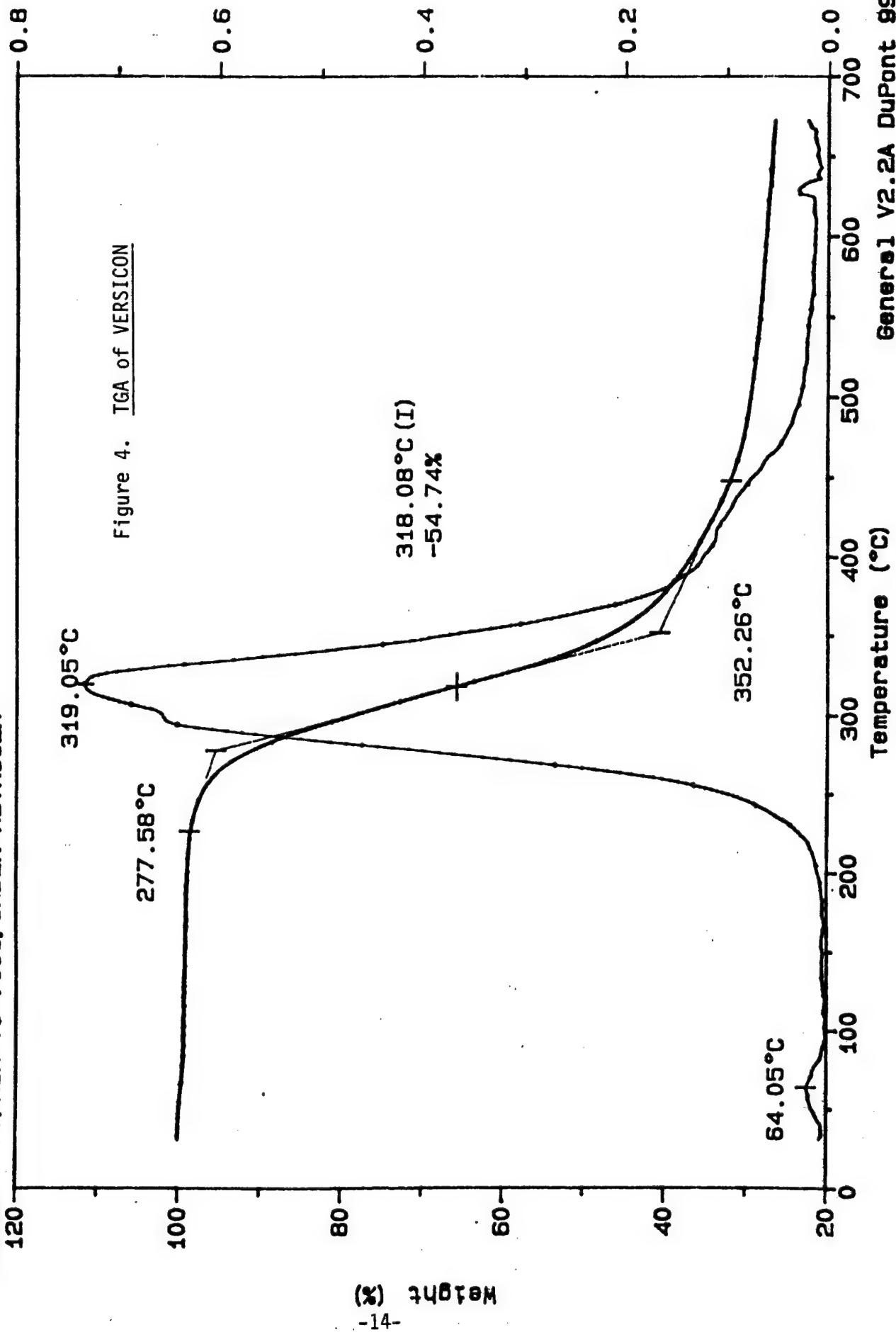


Figure 3. TGA curve of experimental polyaniline sulfosuccinate run under nitrogen

Sample: COMMERCIAL-EB-SALT
Size: 9.3150 mg
Method: KH-TG
Comment: 10/MIN TO 700C. UNDER NITROGEN

TGA



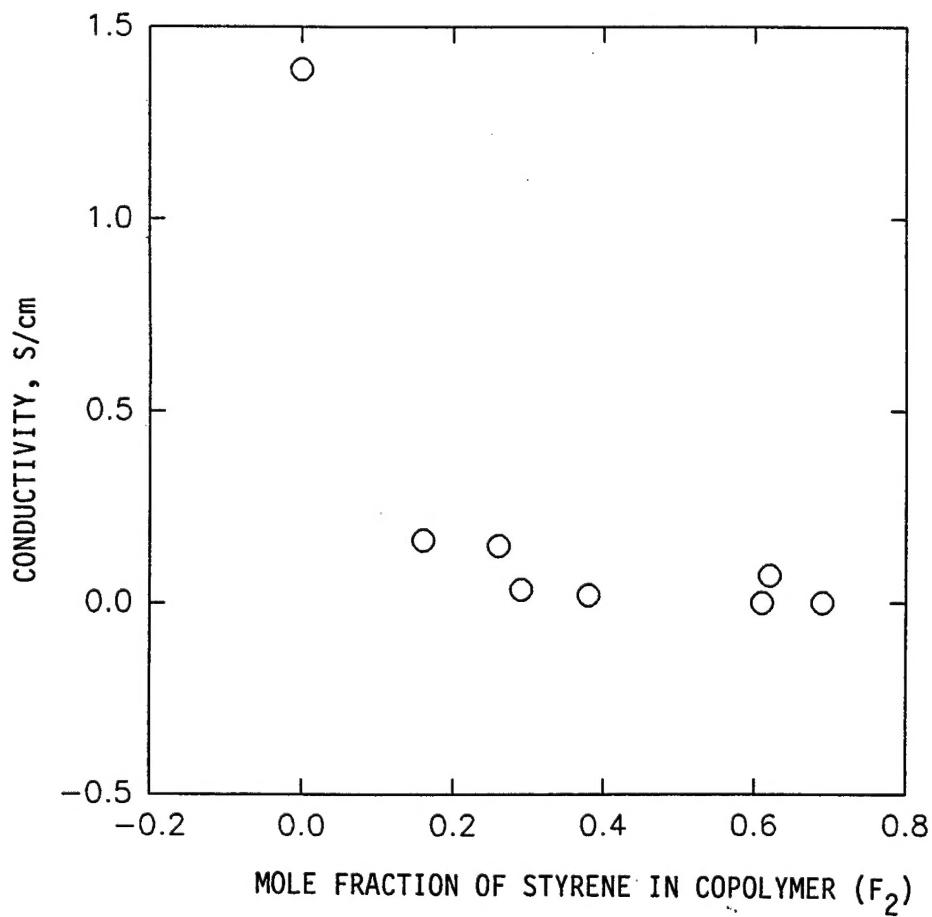


Figure 5. Conductivity versus F_2 for styrene copolymer of aniline.

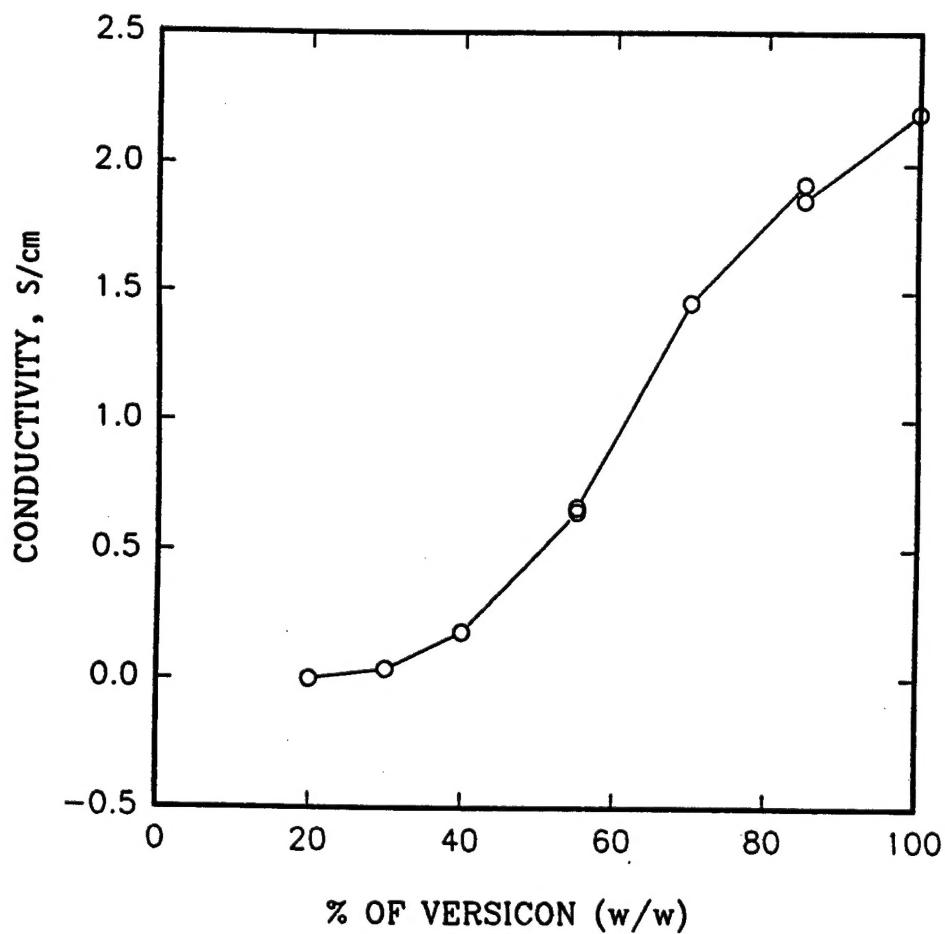
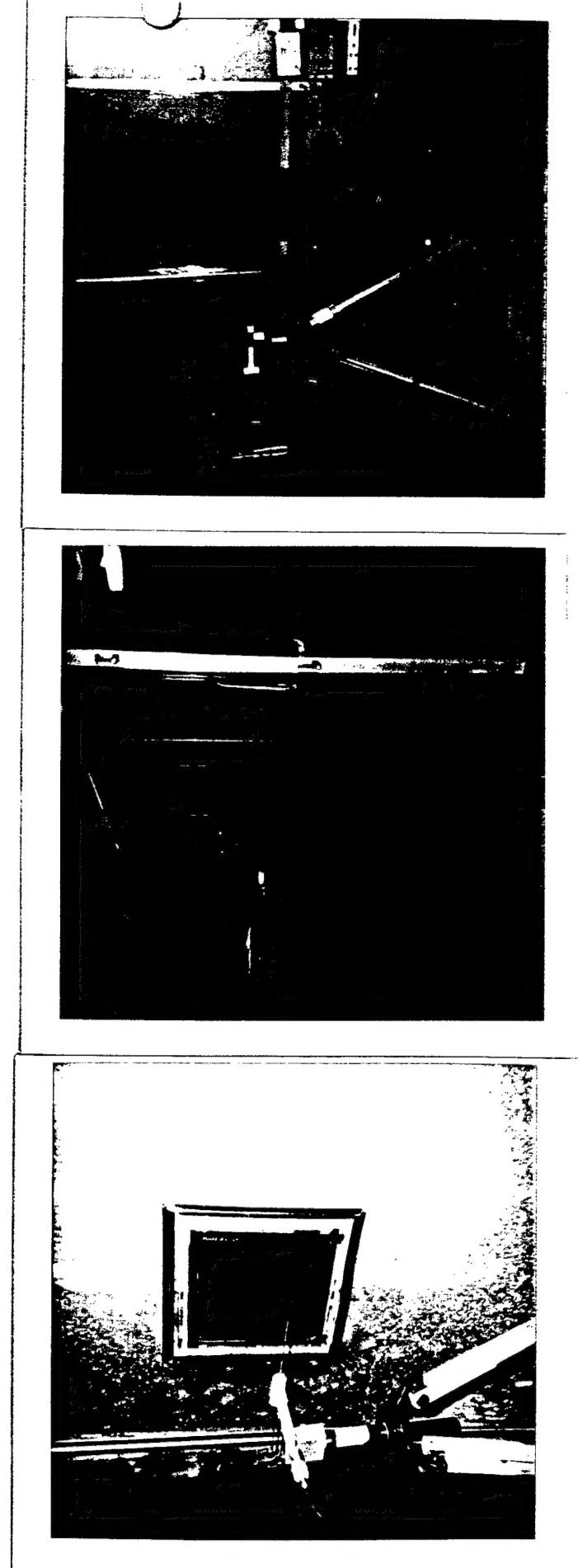


Figure 6. Conductivity versus Composition of blends of Versicon and Polyvinyl Chloride

Figure 7. Photographs of EMI SE Test Set-up



VI. REFERENCES

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VII. CERTIFICATION OF TECHNICAL DATA CONFORMITY

The Contractor, Gumbs Associates, Inc., hereby certifies that, to the best of its knowledge and belief, the technical data delivered herewith under Contract No. DAAK60-93-C-0008 is complete, accurate, and complies with all requirements of the contract.

Ronald W. Gumbs
Ronald W. Gumbs, President

09/08/93
Date